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(54) Title: BATTERY CATHODE

(57) Abstract: Batteries comprising a cathode that includes  $Cu_xM_yO_zX_t$ , where M is a metal, X includes one or more halides and/or  
nitrates, x + y is from about 6.8 to about 7.2, and z and t are selected so that the copper in  $Cu_xM_yO_zX_t$  has a formal oxidation state of  
+2 or greater.

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## BATTERY CATHODE

The invention relates to batteries.

Batteries, such as alkaline batteries, are commonly used as electrical

energy sources. Generally, a battery contains a negative electrode (anode) and a positive  
electrode (cathode). The anode contains an active material (e.g., zinc particles) that can  
be oxidized, and the cathode contains an active material (e.g., manganese dioxide) that  
can be reduced. The active material of the anode is capable of reducing the active  
material of the cathode. In order to prevent direct reaction of the active material of the  
anode and the active material of the cathode, the electrodes are electrically isolated from  
each other by a separator.

When a battery is used as an electrical energy source in a device, such as  
a cellular telephone, electrical contact is made to the electrodes, allowing electrons to  
flow through the device and permitting the respective oxidation and reduction reactions  
to occur to provide electrical power. An electrolyte in contact with the electrodes  
contains ions that flow through the separator between the electrodes to maintain charge  
balance throughout the battery during discharge.

In one aspect, the invention features a battery with a cathode that includes  
 $Cu_xM_yO_zX_t$ , as a cathode active material, in which M is a metal, X includes one or more  
halides and/or nitrate, x + y = 6.8–7.2, and z and t are selected to provide the copper  
with a formal oxidation state of +2 or greater. In some embodiments, the cathode  
includes both  $Cu_xM_yO_zX_t$  and one or more second cathode active material(s), such as  
cupric oxide (CuO), cuprous oxide (Cu<sub>2</sub>O), manganese dioxide (MnO<sub>2</sub>), and/or nickel  
oxyhydroxide (NiOOH). A battery with a cathode that includes  $Cu_xM_yO_zX_t$  can exhibit  
enhanced electrochemical performance (e.g., capacity, open circuit voltage, and/or  
closed circuit voltage) relative to a battery with a cathode that does not include  
 $Cu_xM_yO_zX_t$  (e.g., a battery with a cathode that includes only CuO and/or Cu<sub>2</sub>O as  
cathode active material). Furthermore, a cathode that includes  $Cu_xM_yO_zX_t$  can have a  
higher conductivity than a cathode that does not include  $Cu_xM_yO_zX_t$ .

In another aspect, the invention features a primary battery that includes a  
housing, an anode within the housing, a cathode within the housing, and an alkaline  
electrolyte. The cathode includes one cathode active material (e.g., CuO, MnO<sub>2</sub>,  
NiOOH) and another cathode active material that includes  $Cu_xM_yO_zX_t$ , in which M is a

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metal, X includes one or more halides and/or nitrate, x + y is from about 6.8 to about 7.2, and z and t are selected so that the copper in  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_t$  has a formal oxidation state of +2 or greater.

In another aspect, the invention features a battery that is a closed system and that includes a housing, an anode within the housing, an alkaline electrolyte within the housing, and a cathode within the housing. The cathode has a cathode active material that includes  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_t$ , in which M is a metal, X includes one or more halides and/or nitrate, x + y is from about 6.8 to about 7.2, and z and t are selected so that the copper in  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_t$  has a formal oxidation state of +2 or greater.

In another aspect, the invention features a cathode with a cathode active material including less than about 40 percent by weight  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_t$ , in which M is a metal, X includes one or more halides and/or nitrate, x + y is from about 6.8 to about 7.2, and z and t are selected so that the copper in  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_t$  has a formal oxidation state of +2 or greater.

Embodiments can include one or more of the following features.

M can be indium, gallium, arsenic, scandium, yttrium, bismuth, niobium, calcium, or a lanthanide.

X can be chlorine or nitrate.

In some embodiments, x + y can be about 6.8. In certain embodiments, x + y can be about 7.2.

The copper in  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_t$  can have a formal oxidation state of +2, w, where +2, w is from +2.0 to +2.4 (e.g., from +2.2 to +2.4).

$\text{Cu}_x\text{M}_y\text{O}_z\text{X}_t$  can be  $\text{Cu}_x\text{In}_y\text{O}_z\text{Cl}_t$ ,  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_t$  can be  $\text{Cu}_x\text{In}_y\text{O}_z\text{Cl}_t$ .

The cathode active material can include less than about 35 percent by weight (e.g., less than about 30 percent by weight, less than about 25 percent by weight, less than about 20 percent by weight, less than about 15 percent by weight, less than about ten percent by weight, less than about five percent by weight, less than about two percent by weight, less than about one percent by weight)  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_t$ .

The cathode active material can include more than about 70 percent by weight (e.g., more than about 80 percent by weight, more than about 90 percent by weight, more than about 95 percent by weight, more than about 99 percent by weight)

$\text{Cu}_x\text{M}_y\text{O}_z\text{X}_t$ .

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The cathode can include less than about ten percent by weight graphite (e.g., less than about five percent by weight graphite).

The cathode can include less than about two percent by weight carbon fibers (e.g., less than about 0.5 percent by weight carbon fibers).

The cathode active material can further include a copper oxide (e.g.,  $\text{CuO}$  or  $\text{Cu}_2\text{O}$ ), manganese dioxide, or nickel oxyhydroxide.

The cathode active material can include less than about 20 percent by weight  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_t$  and more than about 80 percent by weight of a copper oxide, manganese dioxide, or nickel oxyhydroxide.

The cathode can have a Coulombic capacity of more than about 260 mAh/gram (e.g., more than about 450 mAh/gram).

The cathode active material can have a resistivity of less than about one Ohm-cm (e.g., less than about  $10^{-2}$  Ohm-cm).

The battery can have an open circuit voltage of more than about 1.2 Volts (e.g., more than about 1.5 Volts).

The battery can have a closed circuit voltage of more than about 1.4 Volts on a load of one mAh/gram of cathode active material. The battery can have a closed circuit voltage of more than about one Volt on a load of ten mAh/gram of cathode active material.

The anode can include zinc.

The electrolyte can be an alkaline electrolyte.

Other aspects, features, and advantages of the invention will be apparent from the drawing, description, and claims.

FIG. 1 is a cross-sectional view of an embodiment of a battery.

FIG. 2 is a portion of an x-ray photoelectron spectrum for  $\text{CuO}$ .

FIG. 2A is a portion of an x-ray photoelectron spectrum for  $\text{Cu}_2\text{O}$ .

FIG. 3 is a graph illustrating discharge curves for  $\text{CuO}$  and  $\text{Cu}_2\text{O}$ .

FIG. 3 is a graph illustrating discharge curves for  $\text{CuO}$  and  $\text{Cu}_2\text{O}$  in a flooded cell at a constant scan rate of 0.02 mV/second.

FIG. 4 is a graph illustrating discharge curves for  $\text{Cu}_2\text{O}$ ,  $\text{InCl}$ ,  $\text{CuO}$ ,  $\text{MnO}_2$ , and  $\text{NiOOH}$ , discharged galvanostatically in a flooded cell at a constant applied current of 110 mA/gram.

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FIG. 5 is a graph illustrating discharge curves for high power electrolytic  $MnO_2$  (curve c),  $CuO$  (curve d), a blend of 90 percent by weight electrolytic  $MnO_2$  and ten percent by weight  $Cu_2O \cdot \frac{1}{2}InCl$  (curve b), and a blend of 90 percent by weight  $CuO$  and ten percent by weight  $Cu_2O \cdot \frac{1}{2}InCl$  (curve a), discharged galvanostatically in a flooded cell at a constant applied current of ten mA/gram.

FIG. 6 is a graph illustrating discharge curves for high power electrolytic  $MnO_2$  (curve a),  $CuO$  (curve d), a blend of 90 percent by weight electrolytic  $MnO_2$  and ten percent by weight  $Cu_2O \cdot \frac{1}{2}InCl$  (curve b), and a blend of 90 percent by weight  $CuO$  and ten percent by weight  $Cu_2O \cdot \frac{1}{2}InCl$  (curve c), discharged galvanostatically in a flooded cell at a constant applied current of 110 mA/gram.

FIG. 7 is a graph illustrating pulse current versus load voltage for a cathode with 100 percent  $CuO$  cathode active material and a cathode with 90 percent  $CuO$  and ten percent  $Cu_2InO_3Cl$  as cathode active material.

FIG. 8 is a graph illustrating polarization curves of fresh AA cells with cathodes that include  $CuO$  and a blend of 90 percent by weight  $CuO$  and ten percent by weight  $Cu_2InO_3Cl$ .

Referring to FIG. 1, a battery or electrochemical cell 10 has a cylindrical housing 18 containing a cathode 12, an anode 14, and a separator 16 between cathode 12 and anode 14. Cathode 12 includes a cathode active material, and anode 14 includes an anode active material. Battery 10 also includes a current collector 20, a seal 22, and a metal top cap 24, which serve as the negative terminal for the battery. Cathode 12 is in contact with housing 18, and the positive terminal of battery 10 is at the end of the battery opposite from the negative terminal. An electrolyte is dispersed throughout battery 10.

The cathode active material preferably includes a copper metal oxyhalide, a copper metal oxynitrate, or a copper metal compound that is both a copper metal oxyhalide and a copper metal oxynitrate. Preferably, the cathode active material includes  $Cu_xM_yO_zX_n$ , where "M" is a metal, "X" includes one or more halides and/or nitrate,  $x+y$  is from about 6.8 to about 7.2 (e.g., about 6.8, about 7.0, about 7.2), and  $z$  and  $n$  are selected to give the copper in  $Cu_xM_yO_zX_n$  a formal oxidation state of +2 or greater. Metal "M" can be a transition metal (e.g., scandium, yttrium, niobium), a lanthanide (e.g., cerium, ytterbium), or a main group metal (e.g., indium, gallium,

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arsenic, bismuth, calcium), "X" can include chlorine, fluorine, bromine, iodine, nitrate, or a combination of one or more halides and/or nitrate. The formal oxidation state of the copper in  $Cu_xM_yO_zX_n$  can be greater than +2 (e.g., +2.33). In some embodiments, the copper in  $Cu_xM_yO_zX_n$  can have a formal oxidation state of +2, in which +2 is from +2.0 to +2.4 (e.g. from +2.2 to +2.4, e.g. +2.3).

In certain embodiments,  $Cu_xM_yO_zX_n$  is  $Cu_xM_yO_zCl_n$ . For example,  $Cu_xM_yO_zX_n$  can be  $Cu_2InO_3Cl$ . The cathode active material can include multiple metals (e.g.,  $Cu_2(In,Ga)_2O_3X_n$ ), and/or a combination of a halide and nitrate (e.g.,  $Cu_xM_yO_z(Cl,(NO_3))_n$ ) and/or a combination of multiple halides and nitrate (e.g.,  $Cu_xM_yO_z(Cl,F,(NO_3))_n$ ).

In some embodiments, the cathode active material of cathode 12 includes from about 0.1 percent by weight to about 100 percent by weight  $Cu_xM_yO_zX_n$ . For example, the cathode active material can include more than about 0.1 percent by weight (e.g., more than about 0.2 percent by weight, more than about 0.5 percent by weight, more than about one percent by weight, more than about two percent by weight, more than about five percent by weight, more than about ten percent by weight, more than about 15 percent by weight, more than about 20 percent by weight, more than about 25 percent by weight, more than about 30 percent by weight, more than about 35 percent by weight, more than about 40 percent by weight, more than about 45 percent by weight, more than about 50 percent by weight, more than about 55 percent by weight, more than about 60 percent by weight, more than about 65 percent by weight, more than about 70 percent by weight, more than about 75 percent by weight, more than about 80 percent by weight, more than about 85 percent by weight, more than about 90 percent by weight, more than about 95 percent by weight, more than about 99 percent by weight, more than about 99.9 percent by weight)  $Cu_xM_yO_zX_n$ . Alternatively or additionally, the cathode active material of cathode 12 can include less than about 100 percent by weight (e.g., less than about 99.9 percent by weight, less than about 99 percent by weight, less than about 95 percent by weight, less than about 90 percent by weight, less than about 85 percent by weight, less than about 80 percent by weight, less than about 75 percent by weight, less than about 70 percent by weight, less than about 65 percent by weight, less than about 60 percent by weight, less than about 55 percent by weight, less than about 50 percent by weight, less than about 45 percent by weight, less than about 40 percent by

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weight, less than about 3.5 percent by weight, less than about 3.0 percent by weight, less than about 2.5 percent by weight, less than about 2.0 percent by weight, less than about 1.5 percent by weight, less than about ten percent by weight, less than about five percent by weight, less than about two percent by weight, less than about one percent by weight, less than about 0.5 percent by weight, less than about 0.2 percent by weight)  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_1$ . In embodiments in which the cathode active material includes less than about 100 percent by weight  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_1$ , the balance of the cathode active material can include at least one other type of cathode active material (other than  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_1$ ). As an example, the cathode active material of cathode 12 can include about ten percent by weight

10  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_1$  and about 90 percent by weight CuO.

In addition to including  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_1$  and, in some embodiments, at least one other cathode active material, cathode 12 includes a conductive aid and a binder.

The conductive aid can increase the electronic conductivity of cathode 12. An example of a conductive aid is graphitic (e.g., graphite particles). In some embodiments, cathode 12 includes less than about ten percent by weight (e.g., less than about nine percent by weight, less than about five percent by weight, less than about two percent by weight, less than about one percent by weight) and/or more than about 0.1 percent by weight (e.g., more than about 0.2 percent by weight, more than about 0.5 percent by weight, more than about 0.8 percent by weight, more than about 0.9 percent by weight) graphitic. Graphitic particles that are used in cathode 12 can be any of the graphite particles used in cathodes. The particles can be synthetic or nonsynthetic, and they can be expanded or nonexpanded. In certain embodiments, the graphite particles are nonsynthetic, nonexpanded graphite particles. In these embodiments, the graphite particles can have an average particle size of less than about 20 microns (e.g., from about two microns to about 12 microns, from about five microns to about nine microns), as measured using a Synpacac HELLIOS analyzer. Nonsynthetic, nonexpanded graphite particles can be obtained from, for example, Brazilian Nacional de Grafite (Itapetirica, MG Brazil) (MP-0702X).

Another example of a conductive aid is carbon fibers, such as those

30 described in commonly assigned U.S.S.N. 09/658,042, filed on September 7, 2000, and entitled "Battery Cathode"; and in U.S. Published Patent Application No. US 2002/0172867 A1, published on November 21, 2002, and entitled "Battery Cathode",

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both of which are hereby incorporated by reference. In some embodiments, cathode 12 can include less than about two percent by weight (e.g., less than about 1.5 percent by weight, less than about one percent by weight, less than about 0.75 percent by weight, less than about 0.5 percent by weight) and/or more than about 0.1 percent by weight (e.g., more than about 0.2 percent by weight, more than about 0.3 percent by weight, more than about 0.4 percent by weight, more than about 0.45 percent by weight) carbon fibers.

In some embodiments, cathode 12 includes from about one percent by weight to about ten percent by weight of one or more total conductive aids.

10 Examples of binders include polyethylene powders, polyacrylamides, Portland cement and fluorocarbon resins, such as polyvinylidene fluoride (PVDF) and polytetrafluoroethylene (PTFE). An example of a polyethylene binder is sold under the trade name Cathylene HA-1681 (available from Hoechst). Cathode 12 may include, for example, from about 0.1 percent to about one percent of binder by weight.

15 In embodiments in which cathode 12 includes  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_1$  as its only cathode active material, cathode 12 can be prepared by disposing (e.g., painting, spraying)  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_1$  on another material or materials. For example,  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_1$  can be disposed on an insulating substrate and/or an electronically conductive substrate. Examples of insulating substrates include glass beads, ceramic pellets, and porous zeolites. Examples of electronically conductive substrates include copper metal and graphitic.

20 In embodiments in which cathode 12 includes  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_1$  and at least one other cathode active material, cathode 12 can be prepared by directly mixing  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_1$  with the other cathode active material(s) (e.g., a copper oxide). In other embodiments, cathode 12 can be prepared by including the other cathode active material(s) in a blend with  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_1$ , in which the other cathode active material(s) can serve as a composite structure or structures. In certain embodiments,  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_1$  can be supported on another material or materials, such as an insulating substrate (e.g., glass beads, ceramic pellets, porous zeolites), an electrochemically active substrate (e.g., CuO), and/or an electronically conductive substrate (e.g., copper metal, graphite). For example,  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_1$  can be coated on a copper oxide material. In some embodiments,  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_1$  can be applied to a copper oxide using sol-gel techniques and/or

precipitation of  $\text{Cu}_2\text{M}_2\text{O}_2\text{X}_4$  from a solution.

As noted above, in certain embodiments, cathode 12 can include both  $\text{Cu}_2\text{M}_2\text{O}_2\text{X}_4$  and at least one other cathode active material. Examples of other cathode active materials include copper oxides (e.g., cupric oxide ( $\text{CuO}$ ), cuprous oxide ( $\text{Cu}_2\text{O}$ )), copper hydroxides (e.g., cupric hydroxide ( $\text{Cu}(\text{OH})_2$ ), cuprous hydroxide ( $\text{Cu}(\text{OH})$ )), cupric iodate ( $\text{Cu}(\text{IO}_3)_2$ ),  $\text{AgCuO}_2$ ,  $\text{LiCuO}_2$ ,  $\text{Cu}(\text{OH})(\text{IO}_3)$ ,  $\text{Cu}_2\text{H}(\text{IO}_3)_2$ ; copper-containing metal oxides or chalcogenides; copper halides (e.g.,  $\text{CuCl}_2$ ); and/or copper manganese oxides (e.g.,  $\text{Cu}(\text{MnO}_4)_2$ ). The copper oxides can be stoichiometric (e.g.,  $\text{CuO}$ ) or non-stoichiometric (e.g.,  $\text{CuO}_x$ , where  $0.5 \leq x \leq 1.5$ ). In some embodiments, cathode 12 can include, in addition to  $\text{Cu}_2\text{M}_2\text{O}_2\text{X}_4$ , from about 0.1 percent to about 99.9 percent, preferably from about 30 percent to about 50 percent, and more preferably from about five percent to about ten percent, of one or more other copper active materials by weight. All weight percentages provided herein that refer to the cathode composition are determined after the electrolyte has been dispersed. Weight percentages that refer to only the cathode active materials (and that are not relative to the overall cathode composition) are determined before the electrolyte has been dispersed.

While copper materials have been described, cathode 12 need not include only copper materials. For example, cathode 12 can include any material that exhibits low solubility (e.g., from about  $10^{-6}$  moles/liter to about  $10^{-1}$  mole/liter) in the system of which it is a part. A soluble cathode material or additive can lower cell performance and shelf life because dissolved ions originating from the cathode material or additive can migrate into the anode and cause premature cell failure. In some embodiments, cathode 12 can include a manganese oxide (e.g.,  $\text{MnO}_2$ , such as EMD); a silver compound (e.g.,  $\text{Ag}_2\text{O}$ ,  $\text{AgO}$ ); a permanganate (e.g.,  $\text{Ba}(\text{MnO}_4)_2$ ,  $\text{AgMnO}_4$ ); nickel oxide; cobalt oxide; and/or nickel oxyhydroxide ( $\text{NiOOH}$ ).

In some embodiments, cathode 12 can include relatively soluble active material, such as  $\text{KMnO}_4$  and/or a ferrate (e.g.,  $\text{K}_2\text{FeO}_4$ ,  $\text{BaFeO}_4$ ). In such embodiments, detrimental interaction between the soluble active material and the cell anode can be limited by the use of a selective and/or ion-trapping separator. Separators are described in, for example, U.S. Patent Application No. 10/682,740, entitled "Battery Separator" and filed on October 9, 2003, which is hereby incorporated by reference. In certain embodiments, detrimental interaction between the soluble active material and the cell

anode can be limited by structuring the cell to have a reserve cell configuration (e.g., structuring the cell to be sea-water activated). Reserve cells are described in, for example, David Linden, *Handbook of Batteries* (McGraw-Hill, 2d ed. 1995), Section III, Ch. 6, which is hereby incorporated by reference. In some embodiments, detrimental interaction between the soluble active material and the cell anode can be limited by adding a material (e.g., a chromate, a permanganate) to the cell that can interact with the cell anode to form a temporary protective film over the anode. The temporary film can protect the anode until the cell becomes electrochemically active.

Cathode 12 can have a relatively high Coulombic capacity. For example, in some embodiments, cathode 12 can have a Coulombic capacity of more than about 250 mAh/gram (e.g., more than about 275 mAh/gram, more than about 300 mAh/gram, more than about 325 mAh/gram, more than about 350 mAh/gram) and/or less than about 610 mAh/gram (e.g., less than about 600 mAh/gram, less than about 500 mAh/gram, less than about 450 mAh/gram, less than about 400 mAh/gram). The Coulombic capacity of a cathode can be measured by effecting a low-rate discharge in a flooded cell, such as that described in Karl V. Kordecsh, *Batteries, Vol. 1: Manganese Dioxide*, (Marcel Dekker, Inc.: New York, 1974), p. 390, Fig. 3.

Alternatively or additionally, the cathode active material in cathode 12 can have a relatively high conductivity. For example, in some embodiments, the cathode active material can have a conductivity of more than about  $10^2 \text{ Ohm}^{-1}\text{cm}^{-1}$  (e.g., more than about  $5 \times 10^2 \text{ Ohm}^{-1}\text{cm}^{-1}$ , more than about  $10^3 \text{ Ohm}^{-1}\text{cm}^{-1}$ , more than about  $5 \times 10^3 \text{ Ohm}^{-1}\text{cm}^{-1}$ , more than about one  $\text{Ohm}^{-1}\text{cm}^{-1}$ , more than about ten  $\text{Ohm}^{-1}\text{cm}^{-1}$ , more than about 100  $\text{Ohm}^{-1}\text{cm}^{-1}$ , more than about 200  $\text{Ohm}^{-1}\text{cm}^{-1}$ , more than about 300  $\text{Ohm}^{-1}\text{cm}^{-1}$ , more than about 400  $\text{Ohm}^{-1}\text{cm}^{-1}$ , more than about 500  $\text{Ohm}^{-1}\text{cm}^{-1}$ , more than about 600  $\text{Ohm}^{-1}\text{cm}^{-1}$ , more than about 700  $\text{Ohm}^{-1}\text{cm}^{-1}$ , more than about 800  $\text{Ohm}^{-1}\text{cm}^{-1}$ , more than about 900  $\text{Ohm}^{-1}\text{cm}^{-1}$ ) and/or less than about  $1,000 \text{ Ohm}^{-1}\text{cm}^{-1}$  (e.g., less than about 900  $\text{Ohm}^{-1}\text{cm}^{-1}$ , less than about 800  $\text{Ohm}^{-1}\text{cm}^{-1}$ , less than about 700  $\text{Ohm}^{-1}\text{cm}^{-1}$ , less than about 600  $\text{Ohm}^{-1}\text{cm}^{-1}$ , less than about 500  $\text{Ohm}^{-1}\text{cm}^{-1}$ , less than about 400  $\text{Ohm}^{-1}\text{cm}^{-1}$ , less than about 300  $\text{Ohm}^{-1}\text{cm}^{-1}$ , less than about 200  $\text{Ohm}^{-1}\text{cm}^{-1}$ , less than about 100  $\text{Ohm}^{-1}\text{cm}^{-1}$ , less than about ten  $\text{Ohm}^{-1}\text{cm}^{-1}$ ). The conductivity of cathode active material can be measured by a 4-probe test method applied to the cathode active material while it is held under pressure.

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Anode 14 can be formed of any of the zinc materials used in battery anodes. For example, anode 14 can be a zinc gel that includes zinc metal particles, a gelling agent, and minor amounts of additives, such as gassing inhibitor. In addition, a portion of the electrolyte is dispersed throughout the anode.

The zinc particles can be any of the zinc particles used in gel anodes.

Examples of zinc particles include those described in U.S. Patent No. 6,284,410 and in U.S. Patent No. 6,521,378, both of which are hereby incorporated by reference. The zinc particles can be a zinc alloy, e.g., containing a few hundred parts per million of indium and bismuth. Anode 14 may include, for example, between 67 percent and 80 percent of zinc particles by weight.

Examples of gelling agents include polyacrylic acids, grafted starch materials, salts of polyacrylic acids, polyacrylates, carboxymethylcellulose or combinations thereof. Examples of such polyacrylic acids are Carbopol 940 and 934 (available from Noveon Inc.) and Polygel 4P (available from 3V). An example of a grafted starch material is Watelock A221 (available from Grain Processing Corporation, Muscatine, IA). An example of a salt of a polyacrylic acid is Alcosorb G1 (available from Ciba Specialties). Anode 14 may include, for example, from about 0.1 percent to about one percent gelling agent by weight.

Gassing inhibitors can be inorganic materials, such as bismuth, tin, lead and indium. Alternatively, gassing inhibitors can be organic compounds, such as phosphate esters, ionic surfactants or nonionic surfactants. Examples of ionic surfactants are disclosed in, for example, U.S. Patent No. 4,777,100, which is hereby incorporated by reference.

Anode 14 can include other materials. For example, in some

embodiments, anode 14 can include metals capable of reducing a cathode containing a copper material. Suitable metals include, e.g., aluminum, magnesium, calcium, silicon, boron, titanium, zirconium, hafnium, lanthanum, manganese, iron, cobalt, chromium, tantalum, and niobium. Binary, ternary, quaternary and other multi-component alloy combinations of these metals, and also those combinations including zinc with these metals, can be used.

The electrolyte can be any of the electrolytes used in batteries. The electrolyte can be aqueous or non-aqueous. An aqueous electrolyte can be an alkaline

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solution, such as an aqueous hydroxide solution, e.g., LiOH, NaOH, KOH, or a mixture of hydroxide solutions (e.g., NaOH/KOH). For example, the aqueous hydroxide solution can include from about 33 percent by weight to about 40 percent by weight of the hydroxide material, such as about 9 N KOH (about 37 percent by weight KOH). In some embodiments, the electrolyte can also include up to about four percent by weight (e.g., about two percent by weight) of zinc oxide.

In some embodiments, the electrolyte can be an aqueous salt solution such as  $ZnCl_2$ ,  $NH_4Cl$ , or a mixture of  $ZnCl_2$  and  $NH_4Cl$ . Other aqueous salt solutions include  $ZnSO_4$ ,  $Zn(ClO_4)_2$ ,  $MgBr_2$ ,  $Mg(ClO_4)_2$ , and seawater.

The electrolyte can include other additives. As an example, the electrolyte can include a soluble material (e.g., an aluminum material) that reduces (e.g., suppresses) the solubility of the cathode active material in the electrolyte. In some embodiments, the electrolyte can include one or more of the following: aluminum hydroxide, aluminum oxide, alkali metal aluminates, aluminum metal, alkali metal halides, alkali metal carbonates, or mixtures thereof. Electrolyte additives are described in commonly assigned U.S.S.N. 10/382,941, filed on March 6, 2003, and entitled "Battery", which is hereby incorporated by reference.

Housing 18 can be any housing commonly used in batteries, e.g., primary alkaline batteries. In some embodiments, housing 18 includes an inner metal wall and an outer electrically non-conductive material such as heat shrinkable plastic. Optionally, a layer of conductive material can be disposed between the inner wall and cathode 12. The layer may be disposed along the inner surface of the inner wall, along the circumference of cathode 12, or both. This conductive layer can be formed, for example, of a carbonaceous material. Such materials include LB1000 (Tiracal), Ecccocot 257 (W.R. Grace & Co.), Electrodag 109 (Adheson Colloids Co.), Electrodag 112 (Adheson) and BB0005 (Adheson). Methods of applying the conductive layer are disclosed in, for example, Canadian Patent No. 1,263,697, which is hereby incorporated by reference.

Current collector 20 can be made from a suitable metal, such as brass. Seal 22 can be made, for example, of nylon.

Battery 10 can be assembled using conventional methods. In some embodiments, cathode 12 can be formed by a pack and drill method, described in

U.S.S.N. 09/645,632, filed on August 24, 2000, and entitled "Battery Cathode", which is hereby incorporated by reference.

In some embodiments, battery 10 can include a hydrogen recombination catalyst to lower the amount of hydrogen gas in the cell, which can be generated, for example, when traces of copper metal are plated onto the anode, causing the rate of hydrogen gas from the zinc anode to increase. Suitable hydrogen recombination catalysts are described, e.g., in U.S. Pat. Nos. 6,500,576, and 3,893,870. Alternatively or in addition, battery 10 can be constructed to include pressure-activated valves or vents, as described, e.g., in U.S. Pat. No. 5,300,371.

In some embodiments in which cathode 12 includes both  $Cu_xM_yO_zX_t$  and at least one other cathode active material, battery 10 can be hermetically sealed such that battery 10 is a closed system. As a comparison, metal air cells and fuel cells are open systems.

In certain embodiments, the cathode active material includes  $(Cu_xM_y)_2M_zO_{2x}$ , where " $M$ " and " $M'$ " are metals, " $X$ " includes one or more halides and/or

nitrate,  $x + y$  is from about 6.8 to about 7.2, and  $z$  and  $t$  are selected to give the copper in  $(Cu_xM_y)_2M_zO_{2x}$  a formal oxidation state of +2 or greater. Examples of metal " $M$ " include nickel, iron, cobalt, and manganese. Metal " $M'$ " can be a transition metal (e.g., scandium, yttrium, niobium), a lanthanide (e.g., cerium, ytterbium), or a main group metal (e.g., indium, gallium, arsenic, bismuth, calcium). " $X$ " can include chloride, fluorine, bromine, iodine, nitrate, or a combination of one or more halides and/or nitrate.

Battery 10 can be, for example, a AA, AAA, AAAA, C, or D battery. In other embodiments, battery 10 can be non-cylindrical, such as coin cell, button cells, prismatic cells, wafer cells, or racetrack-shaped cells. Battery 10 can include a multi-lobed electrode, as described in U.S. Patent No. 6,342,317, which is hereby incorporated by reference.

Battery 10 can be a primary electrochemical cell or a secondary electrochemical cell. Primary cells are meant to be discharged, e.g., to exhaustion, only once, and then discarded. Primary cells are not intended to be recharged. Primary cells are described, for example, in David Linden, Handbook of Batteries (McGraw-Hill, 2d ed. 1993), incorporated above. Secondary electrochemical cells can be recharged for many times, e.g., more than fifty times, more than a hundred times, or more. In some

embodiments, secondary cells can include relatively robust separators, such as separators that have many layers and/or separators that are relatively thick. Secondary cells can also be designed to accommodate for changes, such as swelling, that can occur in the cells. Secondary cells are described, e.g., in Falk & Salkind, "Alkaline Storage Batteries", John Wiley & Sons, Inc. 1969; U.S. Patent No. 345,124; and French Patent No. 164,681, all hereby incorporated by reference.

A battery that includes cathode 12 can have a relatively high closed circuit voltage. For example, the battery can have a closed circuit voltage of more than about 1.1 Volts (e.g., more than about 1.15 Volts, more than about 1.2 Volts, more than about 1.25 Volts, more than about 1.3 Volts) and/or less than about 1.8 Volts (e.g., less than about 1.7 Volts, less than about 1.6 Volts, less than about 1.5 Volts, less than about 1.4 Volts). The closed circuit voltage of a battery can be measured by, for example, applying a six-ampere constant current load to the battery for 0.1 seconds and measuring the voltage of the battery.

A battery that includes cathode 12 can have a relatively high open circuit voltage. For example, the battery can have an open circuit voltage of more than about one Volt (e.g., more than about 1.1 Volts, more than about 1.2 Volts, more than about 1.3 Volts, more than about 1.4 Volts, more than about 1.45 Volts, more than about 1.5 Volts, more than about 1.6 Volts, more than about 1.7 Volts, more than about 1.8 Volts) and/or less than about 1.9 Volts (e.g., less than about 1.8 Volts, less than about 1.7 Volts, less than about 1.6 Volts, less than about 1.5 Volts, less than about 1.4 Volts, less than about 1.3 Volts, less than about 1.2 Volts, less than about 1.1 Volts). The open circuit voltage of a battery can be measured by, for example, a high impedance Voltmeter, with an input impedance of greater than ten MegOhms, so that there is virtually no load on the battery during the test.

The following examples are illustrative, and are not intended to be limiting.

#### EXAMPLES

##### Preparation of $Cu_xIn_yO_zCl_t$

##### Example 1

A  $Cu_xIn_yO_zCl_t$  cathode active material was prepared as follows, based on a method described in Sugise et al., U.S. Patent No. 5,112,783.



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First, 8.07 grams of  $\text{In}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$ , 4.31 grams of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ , and 36.4 grams of  $\text{Cu}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  were dissolved in about 25 milliliters of deionized water. The resulting solution was slowly dried in an alumina crucible over a hot plate at about  $150^\circ\text{C}$ . The dried material was then placed in a furnace and heated in air at  $250^\circ\text{C}$  for 40 minutes. The resulting material was ground and heated at  $425^\circ\text{C}$  for an additional ten minutes. Finally, the product was reground and heated at  $500^\circ\text{C}$  for 30 minutes.

#### Example 2

$\text{Cu}_4\text{InO}_8\text{Cl}$  cathode active material was prepared as follows, based on a modification of a synthesis described in Paranthaman, M. and Steinfeld, H., *J. Solid State Chem.* 1992, 96, 243-246.

Indium metal (2.296 grams),  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (3.41 grams), and  $\text{Cu}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  (24.19 grams) were dissolved in 100 milliliters of dilute nitric acid. The solution was evaporated to dryness. The resulting dry material was then inserted into a preheated furnace at  $500^\circ\text{C}$  for ten minutes, air cooled, and ground. At the final stage, the ground material was reheated at  $500^\circ\text{C}$  for an additional two hours and air cooled.

Analysis of the Example 2  $\text{Cu}_4\text{InO}_8\text{Cl}$  cathode active material by powder x-ray diffraction (XRD) revealed the presence of cubic  $\text{Cu}_4\text{InO}_8\text{Cl}$  as a major phase. Further analysis of the  $\text{Cu}_4\text{InO}_8\text{Cl}$  cathode active material by scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS) confirmed that the ratio of copper to indium was approximately six.

Referring to FIG. 2A, surface analysis of the  $\text{Cu}_4\text{InO}_8\text{Cl}$  cathode active material by x-ray photoelectron spectroscopy (XPS) indicated a copper oxidation state higher than +2. The breadth of the  $2p_{3/2}$  peak for  $\text{Cu}_4\text{InO}_8\text{Cl}$  (FIG. 2A), compared to the breadth of the  $2p_{3/2}$  peak for  $\text{CuO}$  (FIG. 2), was indicative of a high valent copper oxidation state ( $> +2$ ) for  $\text{Cu}_4\text{InO}_8\text{Cl}$ .

The true density of the  $\text{Cu}_4\text{InO}_8\text{Cl}$  cathode active material was measured with a pycnometer under helium atmosphere, and was about  $5.43 \text{ g/cm}^3$ . The resistivity of powder samples of the  $\text{Cu}_4\text{InO}_8\text{Cl}$  was measured under pressure using a four-probe method, and was about  $5 \times 10^3 \text{ Ohm-cm}$ .

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#### Flooded Cell Measurements of $\text{Cu}_4\text{InO}_8\text{Cl}$

FIGS. 3-6 show the electrochemical performance of the Example 2

$\text{Cu}_4\text{InO}_8\text{Cl}$  cathode active material in a flooded cell. By "flooded" it is meant that the  $\text{Cu}_4\text{InO}_8\text{Cl}$  was disposed in an excess of electrolyte while its electrochemical performance was measured. The electrochemical performance of the  $\text{Cu}_4\text{InO}_8\text{Cl}$  was measured under both potentiodynamic conditions (FIG. 3), in which the voltage applied to the  $\text{Cu}_4\text{InO}_8\text{Cl}$  was swept or stepped linearly with time in the negative direction, and galvanostatic conditions (FIGS. 4-6), in which the current applied to the  $\text{Cu}_4\text{InO}_8\text{Cl}$  was constant.

First, measurements of the electrochemical performance of the  $\text{Cu}_4\text{InO}_8\text{Cl}$  and of the  $\text{CuO}$  were taken under potentiodynamic conditions in a flooded cell. Electrochemical characterization of  $\text{Cu}_4\text{InO}_8\text{Cl}$  and of  $\text{CuO}$  was performed in a three electrode double H-glass cell, which included a  $\text{Hg}/\text{HgO}$  reference electrode and a platinum auxiliary electrode. The three-electrode cell also included a working electrode that was prepared by pressing a mixture of 50 percent tetrafluorized acetylene black (TAB) and 50 percent cathode active material mix (total weight =  $100 \pm 0.5 \text{ mg}$ ) onto a nickel x-met current collector using a pressure of one metric ton/cm<sup>2</sup>. To enhance wetting, the working electrode was soaked in electrolyte (9N KOH) for 30 minutes prior to the electrochemical measurements. Voltages applied to the working electrode were stepped in the negative direction at  $0.02 \text{ mV/second}$ , and recorded against the  $\text{Hg}/\text{HgO}$  reference electrode. The recorded voltages were plotted versus the hypothetical zinc reference electrode voltage (assuming  $\text{Zn}/\text{Zn}(\text{OH})_4^{2-}$  as  $1.37 \text{ V}$  negative to  $\text{Hg}/\text{HgO}$ ).

FIG. 3 shows a comparison between the electrochemical performance of  $\text{Cu}_4\text{InO}_8\text{Cl}$  and  $\text{CuO}$  under potentiodynamic conditions. When the electrochemical performance was being evaluated, the potential was shifted negatively from an open-circuit-potential (OCV) down to  $0.400 \text{ V}$  in steps of  $0.02 \text{ mV/second}$ . In FIG. 3, integrated voltammograms, corrected for the reference electrode voltage, show that the  $\text{Cu}_4\text{InO}_8\text{Cl}$  had a higher OCV and higher CCV, down to a  $0.6 \text{ V}$  cut off-voltage, than a comparable electrode with  $\text{CuO}$ . Additionally, the  $\text{Cu}_4\text{InO}_8\text{Cl}$  delivered as much capacity as the  $\text{CuO}$ , to a  $0.6 \text{ V}$  cut-off voltage. Furthermore, for the first 50 percent of the discharge, the  $\text{Cu}_4\text{InO}_8\text{Cl}$  displayed a discharge voltage that was  $200 \text{ mV}$  higher than the discharge voltage of the  $\text{CuO}$ . The  $\text{Cu}_4\text{InO}_8\text{Cl}$  also had a well-defined flat discharge



behavior.

Next, the electrochemical performance of  $\text{Cu}_2\text{InO}_3\text{Cl}$  was evaluated under constant current conditions.

FIG. 4 shows the results of a 110 mA/gram high rate discharge test performed on  $\text{CuO}$ ,  $\text{MnO}_2$ ,  $\text{NiOOH}$ , and  $\text{Cu}_2\text{O}_3\text{InCl}$  under constant current conditions in a flooded cell filled with 9N KOH solution. Reference electrode potentials were corrected to represent the polarization vs. a zinc metal electrode. Relative to commercially available alkaline cathode active materials (e.g., cobalt oxyhydroxide-coated  $\beta\text{-NiOOH}$ , available from Unimcore; electrolytic manganese dioxide (EMD), available from Kerr-McGee),  $\text{Cu}_2\text{InO}_3\text{Cl}$  showed a lower discharge voltage but twice the capacity, to a 0.6 V cut-off. As FIG. 4 shows, at high rate drains (110 mA/gram), the  $\text{Cu}_2\text{O}_3\text{InCl}$  phase showed a good rate capability. In comparison to commercial alkaline  $\text{MnO}_2$  and cobalt oxyhydroxide-coated  $\beta\text{-NiOOH}$  cathode materials,  $\text{Cu}_2\text{O}_3\text{InCl}$  displayed a lower discharge potential but twice the capacity at a 0.6 V cut-off.

FIGS. 5 and 6 show the results of "low rate" and "high rate"

measurements (taken under constant current conditions) of cathode blends that included  $\text{Cu}_2\text{InO}_3\text{Cl}$  and  $\text{CuO}$  or electrolytic  $\text{MnO}_2$  (EMD). Cathode blends containing ten percent by weight  $\text{Cu}_2\text{InO}_3\text{Cl}$  and 90 percent by weight  $\text{CuO}$  or electrolytic  $\text{MnO}_2$  were mixed with an equal amount of tetraionized acetylene black (50/50). The working electrode was prepared as described above. Low rate (ten mA/gram) and high rate (110 mA/gram) discharge tests were performed in a flooded cell filled with 9N KOH solution. Reference electrode potentials were corrected to represent the polarization vs. a zinc metal electrode. The performance of the cathode blends was compared to the performance of high power electrolytic  $\text{MnO}_2$  (HP EMD, from Kerr McGee) and  $\text{CuO}$ . As FIGS. 5 and 6 show, cathode blends including a minor amount of  $\text{Cu}_2\text{InO}_3\text{Cl}$  displayed large improvements in the OCV, CCV, and discharge capacity of  $\text{CuO}$  and high power electrolytic  $\text{MnO}_2$  at both high and low rate drains. A more than three-fold increase in discharge capacity to a 0.6 V cut-off voltage at a 110 mA/gram rate was obtained.

Thus, a small proportion (e.g. ten percent) of  $\text{Cu}_2\text{InO}_3\text{Cl}$  substantially improved the electrochemical performance of  $\text{CuO}$  and electrolytic  $\text{MnO}_2$ , particularly at high rate drains. At a 0.6 V cut-off voltage, blends that included electrolytic  $\text{MnO}_2$  or

$\text{CuO}$  and ten percent  $\text{Cu}_2\text{InO}_3\text{Cl}$  displayed 360 mAh/gram and 620 mAh/gram discharge capacities, respectively. These discharge capacities were approximately three times higher than those of 100 percent electrolytic high power  $\text{MnO}_2$  (100 mAh/gram) and 100 percent  $\text{CuO}$  (230 mAh/gram), at the same discharge rate of 110 mAh/gram.

#### "In Cell" Measurements of $\text{Cu}_2\text{InO}_3\text{Cl}$

In addition to the "flooded" discharge tests, a second type of test was run on "spring-loaded cells" that approximated coin cell configurations and that could maintain good contact by use of a constant pressure spring. The spring-loaded cells contained  $\text{CuO}$  or blends including  $\text{Cu}_2\text{InO}_3\text{Cl}$ .

The cells were constructed so as to approximate the construction of a AA cell, as described below.

#### Preparation of Cathode

The cathode blend included 95 percent by weight positive active material, 4.8 percent by weight expanded graphite (Tinner-E-BNB90, from Tinnel), and 0.2 percent by weight binder (Coatylene HA, 1681 Polyethylene Powder, from Hoechst).

A pressed cathode pellet was prepared from the cathode blend, and had the following dimensions: a thickness of 1.7 mm, a diameter of 17.8 mm, and a volume of 423  $\text{mm}^3$ . The cathode had a weight of 1.4 grams.

The cathode pellet was soaked in 9N KOH electrolyte via vacuum back-filling, thereby absorbing about 0.2 grams of electrolyte.

#### Preparation of Anode

An anode pellet was formed by pressing about six grams of a 70 percent zinc slurry in a 17.8 mm die at 0.8 metric ton pressure, and pressing out a portion of the gelled electrolyte. The porous zinc pellet, retrieved after pressing out the excess electrolyte, was employed as the anode in the spring-loaded cell.

The starting composition of the zinc slurry (before pressing) was as follows: 35 percent by weight Duracell Enhanced Zinc Powder (containing 230 ppm bismuth, 150 ppm indium), 35 percent by weight Noranda grade P25 Fine Zinc Powder, 29.4 percent by weight 40/2 Electrolyte Solution (containing 34.7% KOH, 2.0%  $\text{ZnO}$ , balance water), 0.43 percent by weight Carbolpol PAA 940 Gellant, 0.03 percent by weight Waterlock Gellant A221, 0.005 percent by weight (based on total slurry weight) RM 510 Organic Gassing Inhibitor, and 0.03 percent by weight (based on total slurry

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weight) chemically plated indium metal gassing inhibitor.

#### Separator

A three-layer separator was employed. The separator included an outer 23-micron cellophane layer and an outer 54-micron poly(vinyl alcohol)-based non-woven layer (PA25MC). The separator further included a third copper-trapping layer that was sandwiched between the two outer layers. The third copper-trapping layer included -325 mesh bismuth powder and a poly(acrylic acid) adhesive. The separator was sealed along its circumference with a Teflon-encapsulated O-ring. Thus, all electrolyte diffusion and migration between the cathode and the anode was forced to pass through the copper-trapping layer in order to minimize copper ion transfer from cathode to anode. Separators are further described in U.S. Patent Application No. 10/682,740, incorporated above.

#### Results

The cells were subjected to a series of short current pulses (from about ten milliamperes to about one ampere) of increasing intensity with a 15-minute rest (zero current) in between pulses. Closed Circuit Voltage (CCV) was then observed during the duration of the pulse and the CCV at the end of the pulse was plotted against the discharge intensity. Thus the ability of each material or blend of materials to support increasingly heavier discharge intensities was determined. A higher CCV indicated that the material could support a heavier discharge intensity.

FIG. 7 shows the results from the "spring-loaded cell" tests. With the addition of ten 10 percent  $\text{Cu}_2\text{InO}_6\text{Cl}$  to the cathode (the remaining 90 percent being  $\text{CuO}$ ), CCV was consistently higher, at all levels of discharge intensity, relative to a cathode with 100 percent  $\text{CuO}$  cathode active material. At a typical cut-off voltage of 0.8 V, the  $\text{Cu}_2\text{InO}_6\text{Cl}$  containing cell could support a 300 mA/gram active current, which was twice that of the cell that contained only  $\text{CuO}$  (i.e., that did not contain any  $\text{Cu}_2\text{InO}_6\text{Cl}$ ).

#### Assembled AA Cell Measurements

A third type of test was run on fully assembled AA alkaline cells. These cells were constructed as follows.

#### Preparation of Cathode

The cathode included 89.3 percent by weight positive active material, 4.5

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percent by weight graphite (NDG Grafmax MP12), six percent by weight 9N KOH electrolyte, and 0.2 percent by weight Coathylene HA-1681 Polyethylene Powder Binder.

Cathode pellets were prepared with the following dimensions: a height of 42.5 mm, an outer diameter of 13.3 mm, and an inner diameter of 9.9 mm. The cathode had a volume of 2660  $\text{mm}^3$ , and a weight of 10.3 grams.

#### Preparation of Anode

The anode included 75 percent by weight zinc powder (containing 230 ppm bismuth, 150 ppm indium), 24 percent by weight electrolyte (40/2 KOH solution), 0.3 percent by weight Carbolopol PAA 940, 0.02 percent by weight Watlock Geliant A211, 0.005 percent by weight (based on total slurry weight) RM 510 Organic Gassing Inhibitor, and 0.03 percent by weight (based on total slurry weight) chemically plated indium metal gassing inhibitor. Furthermore, 0.6 gram of 9N KOH electrolyte preshot was added to the cathode prior to anode metering.

#### Separator

A Duralum 225 tube and disc separator was used. The tube was 40 mm high and had an outer diameter of 9.8 mm. The disc had a flattened total diameter of 15 mm and a cupped internal diameter of 9.8 mm. The sidewall height of the disc was 2.5 mm. The seams of the separator overlapped without sealing. There was no copper trapping layer used between the non-woven and cellophane layers of the Duralum separator.

#### Results

Fresh AA cells were evaluated by a signature test, which involved applying increments of current (from about 50 milliamperes to about one ampere) and measuring the response in voltages (FIG. 8). A fresh cell has not been subjected to any discharge other than the discharge that occurs during routine electrical inspection. As FIG. 8 shows, the AA cells containing  $\text{CuO}$  with a minor amount of  $\text{Cu}_2\text{InO}_6\text{Cl}$  (ten percent by weight) were more rate capable than the cells containing 100 percent  $\text{CuO}$  as a cathode. The AA cells containing ten percent by weight  $\text{Cu}_2\text{InO}_6\text{Cl}$  could sustain currents up to 500 mA, while the closed circuit voltage was measured as approximately 0.7 V. On the other hand, the AA cells with 100 percent  $\text{CuO}$  performed poorly at high drain rates, displaying a sharp drop in the cell voltages. Additionally, the cells with ten

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10 percent by weight  $\text{Cu}_2\text{InO}_4\text{Cl}$  showed higher OCV and CCV at low and high drain rates.

All references, such as patent applications, publications, and patents, referred to herein are incorporated by reference in their entirety.

Other embodiments are in the claims.

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## CLAIMS

1. A battery, comprising:  
a housing;  
an anode within the housing;  
an electrolyte within the housing; and  
a cathode within the housing, the cathode including a cathode active material comprising less than about 40 percent by weight  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_t$ , wherein M is a metal, X includes one or more halides and/or nitrate,  $x + y$  is from about 6.8 to about 7.2, and z and t are selected so that the copper in  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_t$  has a formal oxidation state of +2 or greater.
2. The battery of claim 1, wherein M is indium, gallium, arsenic, scandium, yttrium, bismuth, niobium, calcium, or a lanthanide.
3. The battery of claim 1, wherein M is indium.
4. The battery of claim 1, wherein X is chlorine.
5. The battery of claim 1, wherein  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_t$  is  $\text{Cu}_2\text{In}_y\text{O}_z\text{Cl}_t$ .
6. The battery of claim 1, wherein  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_t$  is  $\text{Cu}_2\text{InO}_6\text{Cl}$ .
7. The battery of claim 1, wherein the cathode active material comprises less than about 35 percent by weight  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_t$ .
8. The battery of claim 1, wherein the cathode active material comprises less than about 30 percent by weight  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_t$ .
9. The battery of claim 1, wherein the cathode active material comprises less than about 25 percent by weight  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_t$ .
10. The battery of claim 1, wherein the cathode active material comprises less than about 20 percent by weight  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_t$ .
11. The battery of claim 1, wherein the cathode active material comprises less than about 15 percent by weight  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_t$ .
12. The battery of claim 1, wherein the cathode active material comprises less than about ten percent by weight  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_t$ .
13. The battery of claim 1, wherein the cathode active material comprises less than about five percent by weight  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_t$ .
14. The battery of claim 1, wherein the cathode active material comprises less than about two percent by weight  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_t$ .

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15. The battery of claim 1, wherein the cathode active material comprises less than about one percent by weight  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_t$ .
16. The battery of claim 1, wherein  $x + y$  is about 6.8.
17. The battery of claim 1, wherein  $x + y$  is about 7.2.
18. The battery of claim 1, wherein the copper in  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_t$  has a formal oxidation state of +2,  $w$  and +2,  $w$  is from +2.0 to +2.4.
19. The battery of claim 1, wherein the copper in  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_t$  has a formal oxidation state of +2,  $w$  and +2,  $w$  is from +2.2 to +2.4.
20. The battery of claim 1, wherein the cathode comprises less than about ten percent by weight graphite.
21. The battery of claim 1, wherein the cathode comprises less than about five percent by weight graphite.
22. The battery of claim 1, wherein the cathode comprises less than about two percent by weight carbon fibers.
23. The battery of claim 1, wherein the cathode comprises less than about 0.5 percent by weight carbon fibers.
24. The battery of claim 1, wherein the cathode active material further comprises a copper oxide, manganese dioxide, or nickel oxyhydroxide.
25. The battery of claim 1, wherein the cathode active material further comprises a copper oxide.
26. The battery of claim 25, wherein the copper oxide comprises  $\text{CuO}$  or  $\text{Cu}_2\text{O}$ .
27. The battery of claim 1, wherein the cathode active material comprises less than about 20 percent by weight  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_t$  and more than about 80 percent by weight of a copper oxide, manganese dioxide, or nickel oxyhydroxide.
28. The battery of claim 1, wherein the cathode active material comprises less than about 20 percent by weight  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_t$  and more than about 80 percent by weight of a copper oxide.
29. The battery of claim 1, wherein the cathode has a Coulombic capacity of more than about 260 mAh/gram.
30. The battery of claim 1, wherein the cathode has a Coulombic capacity of more than about 450 mAh/gram.

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31. The battery of claim 1, wherein the cathode active material has a resistivity of less than about one Ohm-cm.
32. The battery of claim 1, wherein the cathode active material has a resistivity of less than about  $10^2$  Ohm-cm.
33. The battery of claim 1, wherein the battery has an open circuit voltage of more than about 1.2 Volts.
34. The battery of claim 1, wherein the battery has an open circuit voltage of more than about 1.5 Volts.
35. The battery of claim 1, wherein the battery has a closed circuit voltage of more than about 1.4 Volts on a load of one mA/gram of cathode active material.
36. The battery of claim 1, wherein the battery has a closed circuit voltage of more than about one Volt on a load of ten mA/gram of cathode active material.
37. The battery of claim 1, wherein the anode comprises zinc.
38. The battery of claim 1, wherein the electrolyte is an alkaline electrolyte.
39. A battery, comprising:  
a housing;  
an anode within the housing;  
a cathode within the housing, the cathode including a first cathode active material and a second cathode active material comprising  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_t$ , wherein  $M$  is a metal,  $X$  includes one or more halides and/or nitrate,  $x + y$  is from about 6.8 to about 7.2, and  $z$  and  $t$  are selected so that the copper in  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_t$  has a formal oxidation state of +2 or greater; and  
an alkaline electrolyte,  
wherein the battery is a primary battery.
40. The battery of claim 39, wherein the first cathode active material is  $\text{CuO}$ ,  $\text{MnO}_2$  or  $\text{NiOOH}$ .
41. The battery of claim 39, wherein the anode comprises zinc.
42. The battery of claim 39, wherein  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_t$  is  $\text{Cu}_2\text{M}_y\text{O}_z\text{Cl}_t$ .
43. The battery of claim 39, wherein  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_t$  is  $\text{Cu}_2\text{InO}_4\text{Cl}$ .
44. A battery, comprising:  
a housing;  
an anode within the housing;

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- an alkaline electrolyte within the housing, and  
a cathode within the housing, the cathode including a cathode active material comprising  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_t$ , wherein M is a metal, X includes one or more halides and/or nitrate,  $x + y$  is from about 6.8 to about 7.2, and  $z$  and  $t$  are selected so that the copper in  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_t$  has a formal oxidation state of +2 or greater, wherein the battery is a closed system.
45. The battery of claim 44, wherein M is indium, gallium, arsenic, scandium, yttrium, bismuth, niobium, calcium, or a lanthanide.
46. The battery of claim 44, wherein M is indium.
47. The battery of claim 44, wherein X is chlorine.
48. The battery of claim 44, wherein  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_t$  is  $\text{Cu}_2\text{In}_2\text{O}_7\text{Cl}_2$ .
49. The battery of claim 44, wherein  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_t$  is  $\text{Cu}_2\text{InO}_6\text{Cl}$ .
50. The battery of claim 44, wherein the cathode active material comprises more than about 70 percent by weight  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_t$ .
51. The battery of claim 44, wherein the cathode active material comprises more than about 80 percent by weight  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_t$ .
52. The battery of claim 44, wherein the cathode active material comprises more than about 90 percent by weight  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_t$ .
53. The battery of claim 44, wherein the cathode active material comprises more than about 95 percent by weight  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_t$ .
54. The battery of claim 44, wherein the cathode active material comprises more than about 99 percent by weight  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_t$ .
55. The battery of claim 44, wherein  $x + y$  is about 6.8.
56. The battery of claim 44, wherein  $x + y$  is about 7.2.
57. The battery of claim 44, wherein the copper in  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_t$  has a formal oxidation state of +2,  $w$  and +2,  $w$  is from +2.0 to +2.4.
58. The battery of claim 44, wherein the copper in  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_t$  has a formal oxidation state of +2,  $w$  and +2,  $w$  is from +2.2 to +2.4.
59. The battery of claim 44, wherein the battery has an open circuit voltage of more than about 1.2 Volts.
60. The battery of claim 44, wherein the battery has an open circuit voltage of more than about 1.5 Volts.

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61. The battery of claim 44, wherein the battery has a closed circuit voltage of more than about 1.4 Volts on a load of one mA/gram of cathode active material.
62. The battery of claim 44, wherein the battery has a closed circuit voltage of more than about one Volt on a load of ten mA/gram of cathode active material.
63. The battery of claim 44, wherein the anode comprises zinc.
64. A cathode including a cathode active material comprising less than about 40 percent by weight  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_t$ , wherein M is a metal, X includes one or more halides and/or nitrate,  $x + y$  is from about 6.8 to about 7.2, and  $z$  and  $t$  are selected so that the copper in  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_t$  has a formal oxidation state of +2 or greater.
65. The cathode of claim 64, wherein M is indium, gallium, arsenic, scandium, yttrium, bismuth, niobium, calcium, or a lanthanide.
66. The cathode of claim 64, wherein M is indium.
67. The cathode of claim 64, wherein X is chlorine.
68. The cathode of claim 64, wherein  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_t$  is  $\text{Cu}_2\text{In}_2\text{O}_7\text{Cl}_2$ .
69. The cathode of claim 64, wherein  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_t$  is  $\text{Cu}_2\text{InO}_6\text{Cl}$ .
70. The cathode of claim 64, wherein the cathode active material comprises less than about 35 percent by weight  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_t$ .
71. The cathode of claim 64, wherein the cathode active material comprises less than about 30 percent by weight  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_t$ .
72. The cathode of claim 64, wherein the cathode active material comprises less than about 25 percent by weight  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_t$ .
73. The cathode of claim 64, wherein the cathode active material comprises less than about 20 percent by weight  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_t$ .
74. The cathode of claim 64, wherein the cathode active material comprises less than about 15 percent by weight  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_t$ .
75. The cathode of claim 64, wherein the cathode active material comprises less than about ten percent by weight  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_t$ .
76. The cathode of claim 64, wherein the cathode active material comprises less than about five percent by weight  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_t$ .
77. The cathode of claim 64, wherein the cathode active material comprises less than about two percent by weight  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_t$ .
78. The cathode of claim 64, wherein  $x + y$  is about 6.8.

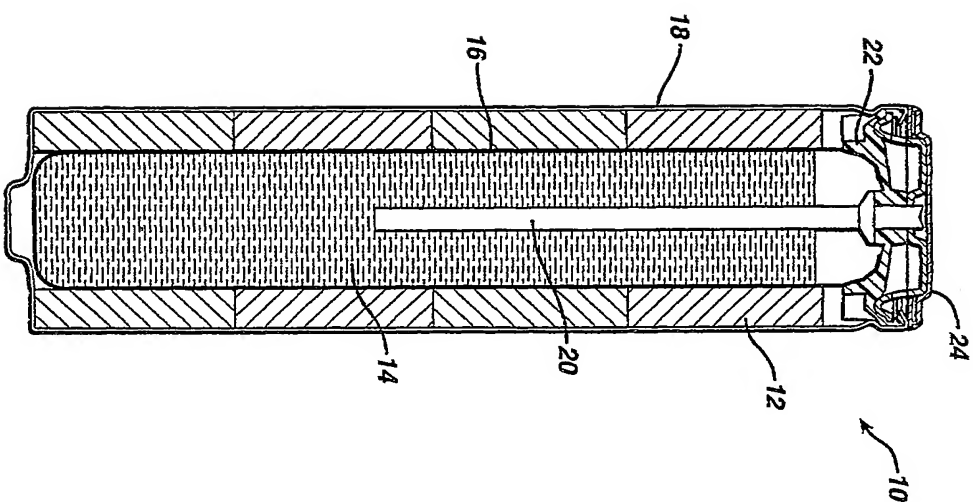
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79. The cathode of claim 64, wherein  $x + y$  is about 7.2.

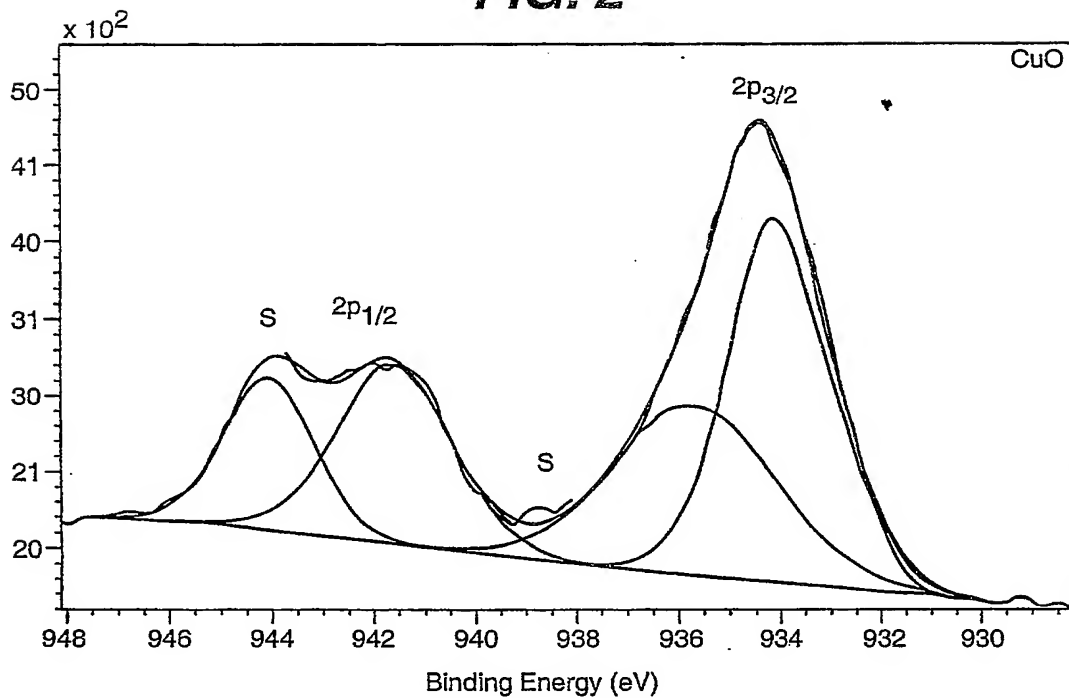
80. The cathode of claim 64, wherein the copper in  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_4$  has a formal oxidation state of +2,  $w$  and +2,  $w$  is from +2.0 to +2.4.

81. The cathode of claim 64, wherein the copper in  $\text{Cu}_x\text{M}_y\text{O}_z\text{X}_4$  has a formal oxidation state of +2,  $w$  and +2,  $w$  is from +2.2 to +2.4.

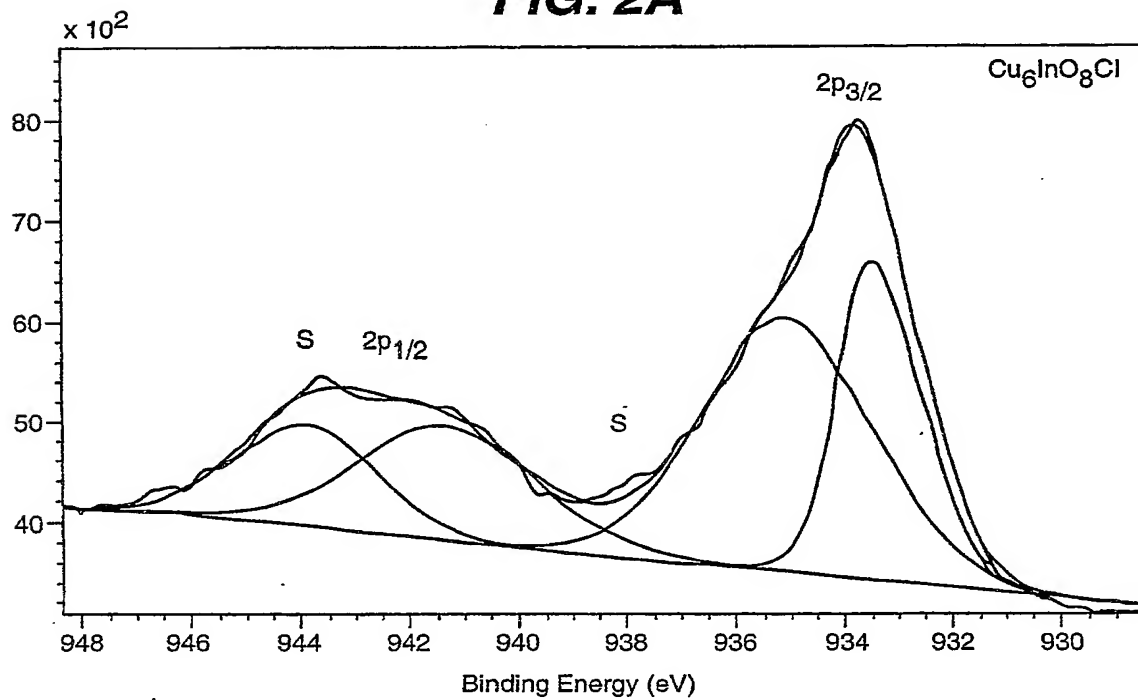
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**FIG. 1**

**FIG. 2**



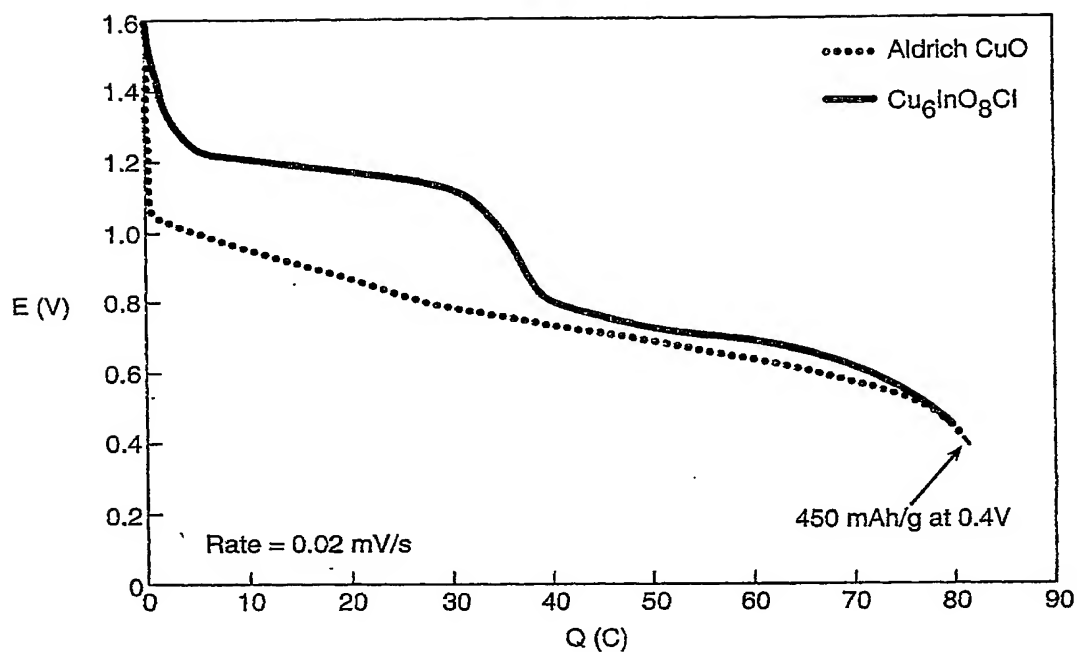
**FIG. 2A**



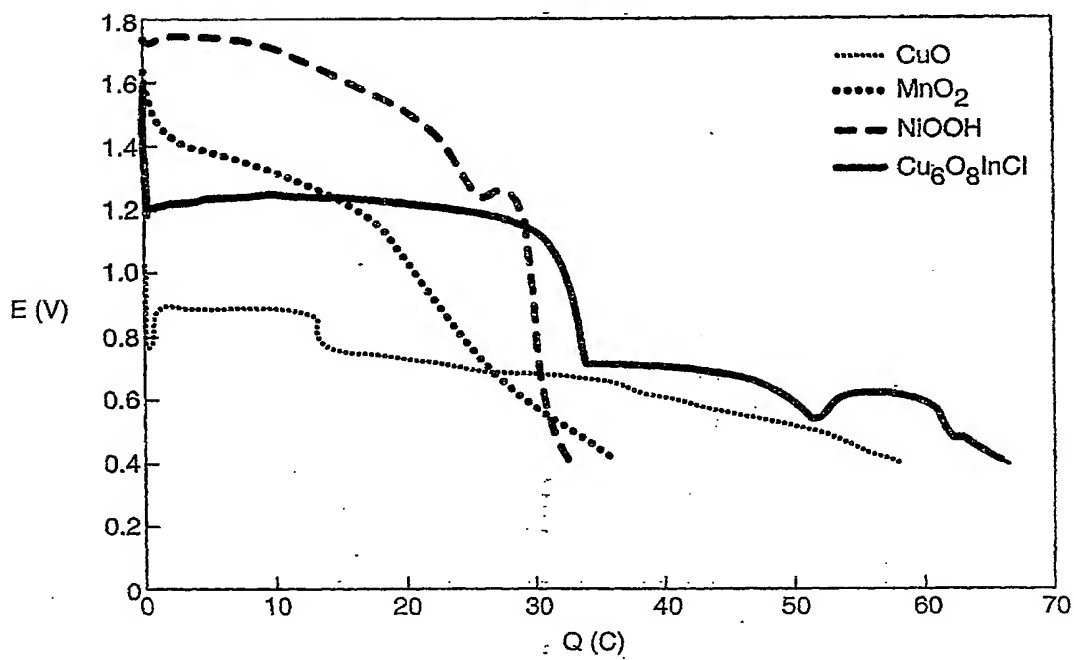


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**FIG. 3**



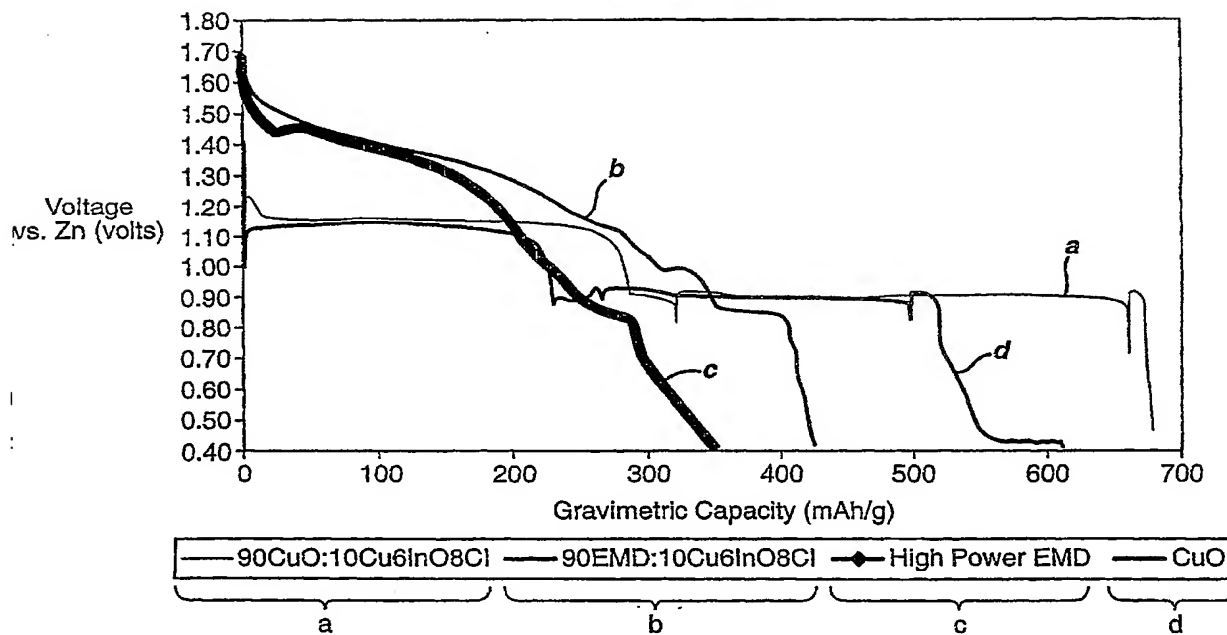
**FIG. 4**



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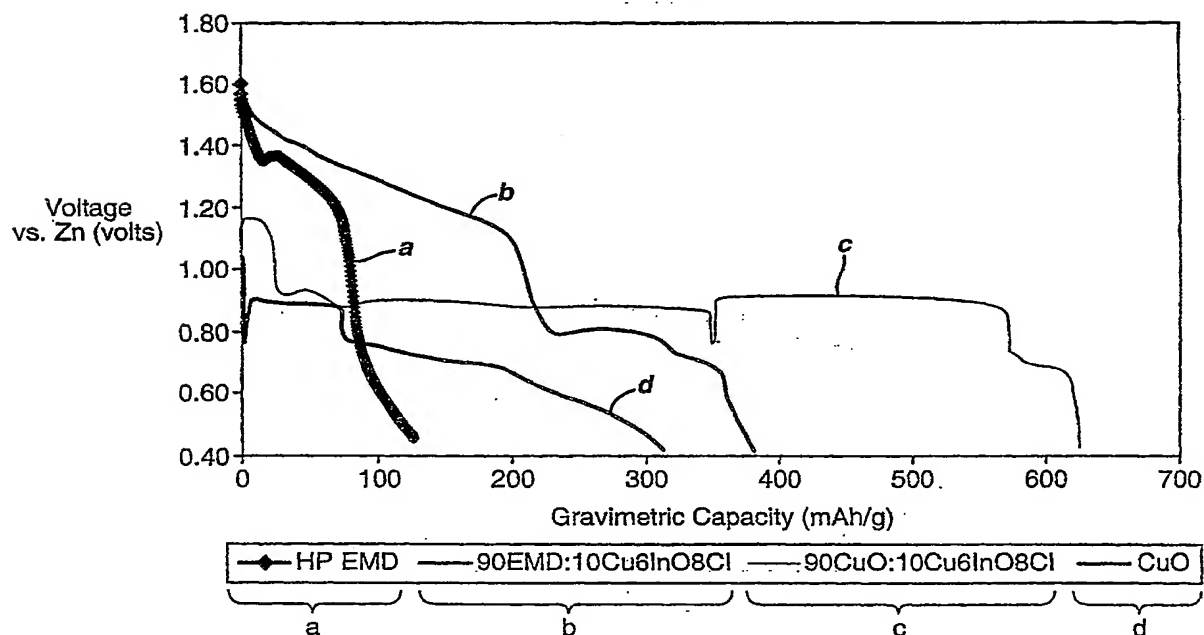
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**FIG. 5**

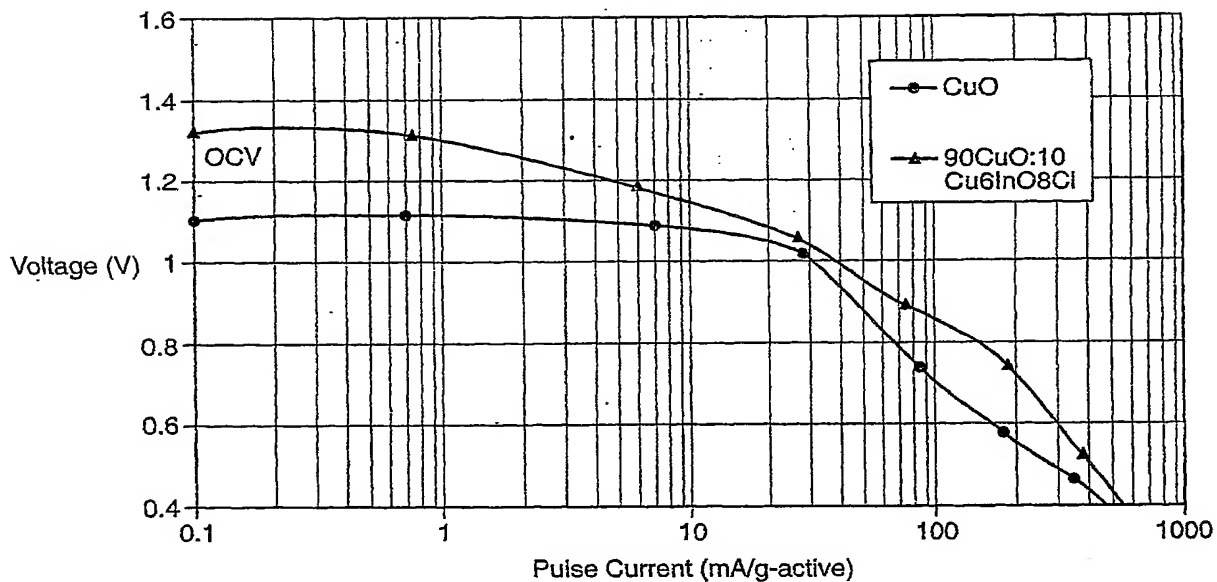


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**FIG. 6**



**FIG. 7**



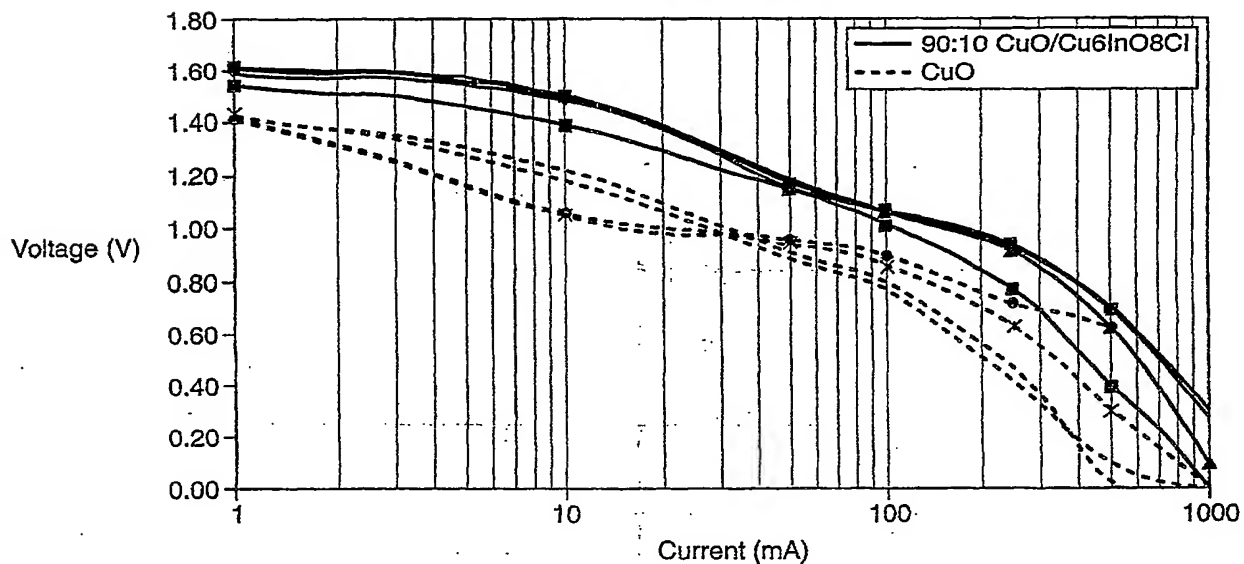
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**FIG. 8**



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WO 2005/064709

PCT/US2004/042851

## INTERNATIONAL SEARCH REPORT

Intern  
PCT/US2004/042851A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 H01M4/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELD(S) SEARCHED  
Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	M. PARANTHAMAN AND H. STEINFINK: J. SOLID STATE CHEMISTRY, vol. 96, 1992, pages 243-246, XP009046260 the whole document	1-81
X	US 5 112 783 A (SUBISE ET AL) 12 May 1992 (1992-05-12) column 1, lines 13,14; claims 1-6	1-81
A	PATENT ABSTRACTS OF JAPAN vol. 005, no. 153 (E-076), 26 September 1981 (1981-09-26) & JP 56 086464 A (SANYO ELECTRIC CO LTD), 14 July 1981 (1981-07-14) abstract	1-81

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## Special categories of cited documents:

- \* document defining the general state of the art which is not  
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Date of the actual completion of the international search

Date of mailing of the international search report

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## INTERNATIONAL SEARCH REPORT

Intern  
PCT/US2004/042851

## C. (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 012, no. 447 (E-685), 24 November 1988 (1988-11-24) & JP 63 174270 A (SANYO ELECTRIC CO LTD), 18 July 1988 (1988-07-18) abstract	1-81

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## INTERNATIONAL SEARCH REPORT

International Application No.  
PCT/US2004/042851

## Box II Observations where certain claims were found unsearchable (Continuation of Item 2 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(e) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.:  
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:  
see FURTHER INFORMATION sheet PCT/ISA/210

3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(e).

## Box III Observations where unity of invention is lacking (Continuation of Item 3 of first sheet)

This International Searching Authority found multiple inventions in this International application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, the International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.  
☐ No protest accompanied the payment of additional search fees.

Form PCT/ISA/210 (Continuation of first sheet (2)) (January 2004)

## FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

International Application No. PCT/US2004/042851

## Continuation of Box II.2

Claims Nos.: -

Present independent claims 1,39,44,64 relate to an extremely large number of possible compounds CuxMyOzXt, where M is a metal. Support within the meaning of Article 6 PCT and disclosure within the meaning of Article 5 PCT is to be found, however, for only a very small proportion of the compounds claimed. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Consequently, the search has been carried out for those parts of the claims which appear to be supported and disclosed, namely those parts relating to the compounds according to claim 2.

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO guideline C-VI, 8.5), should the problems which led to the Article 17(2) declaration be overcome.

INTERNATIONAL SEARCH REPORT

Intern application No  
PCT/US2004/042851

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5112783	A	12-05-1992	JP
		2979515 B2	15-11-1999
		JP 3218921 A	26-09-1991
		2967541 B2	25-10-1999
		JP 3279254 A	10-12-1991
		DE 4101761 A1	14-08-1991
JP 56086464	A	14-07-1981	NONE
JP 63174270	A	18-07-1988	NONE